



# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material<sup>®</sup> 674b

#### X-Ray Powder Diffraction Intensity Set for Quantitative Analysis by X-Ray Powder Diffraction

This Standard Reference Material (SRM) consists of four oxide powders intended primarily for use as internal standards for quantitative X-ray diffraction analysis. The powders are ZnO (wurtzite structure), TiO<sub>2</sub> (rutile structure), Cr<sub>2</sub>O<sub>3</sub> (corundum structure), and CeO<sub>2</sub> (fluorite structure). These four oxides offer a range of linear attenuations for Cu-K $\alpha$  radiation: 279 cm<sup>-1</sup>, 536 cm<sup>-1</sup>, 912 cm<sup>-1</sup>, and 2203 cm<sup>-1</sup>, respectively, that allow the user to nominally match that of standard to the unknown in order to minimize the effects of microabsorption. A unit of SRM 674b consists of approximately 10 g of each powder, bottled in an argon atmosphere.

**Material Description:** The powders consist of fine-grained high-purity equi-axial grains that are not in an aggregated state. The isometric form of the grains effectively eliminates preferred orientation effects in these powders. The de-aggregated state of these materials ensures the homogeneity of test mixtures prepared by conventional methods.

An analysis of the lattice parameters and phase fractions determined from X-ray powder diffraction data collected from mixtures of SRM 674b and SRM 676 [1] indicated that the SRM material was homogeneous with respect to diffraction properties.

**Certified Values and Uncertainties:** The certified phase purity of these materials, expressed as a mass fraction is given in Table 1.

Table 1. Phase Purity and Uncertainty

Crystalline Component	Phase Purity
ZnO	95.28 % $\pm$ 0.64 %
TiO <sub>2</sub>	89.47 % $\pm$ 0.62 %
Cr <sub>2</sub> O <sub>3</sub>	95.91 % $\pm$ 0.60 %
CeO <sub>2</sub>	91.36 % $\pm$ 0.55 %

The interval defined by the certified value and its uncertainty represents an expanded uncertainty using  $k = t$ , where  $t$  is the appropriate 2-sided 95% confidence interval coefficient, in the absence of systematic error [2,3]. The uncertainty reported does not include that of the phase purity determination of the standard used for this certification: SRM 676.

**Expiration of Certification:** The certification of this SRM is valid indefinitely within the stated measurement uncertainties, provided the SRM is stored and handled in accordance with the "Storage" section of this certificate.

**Maintenance of SRM Certification:** NIST will monitor this SRM over the period of its certification. If substantive changes occur that affect the certification, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The technical direction and overall coordination on the certification of this SRM were provided by J.P. Cline of the NIST Ceramics Division.

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Certificate Issue Date: 21 September 2005

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The material preparation, measurements, and data analysis leading to the certification of this SRM were performed by R.S. Winburn of Minot State University, Minot, ND, J.P. Cline of the NIST Ceramics Division and R.B. Von Dreele of Argonne National Laboratory, Argonne, IL.

Statistical analysis was provided by J.J. Filliben and Ivelisse Aviles of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

**Materials:** The ZnO and TiO<sub>2</sub> powders of SRM 674b were obtained from Alfa Aesar<sup>1</sup>, Ward Hill, MA, while the Cr<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> powders were obtained from Cerac Inc., Milwaukee, WI.

**Certification:** The oxide powders of this SRM were certified with respect to the mass fraction of material that exhibits Bragg scattering in correspondence to their crystal structure, or phase purity. The certification procedure utilized Quantitative Rietveld Analyses (QRA) [4] (for a complete discussion of the Rietveld method, see [5,6]) of neutron time-of-flight (TOF) diffraction measurements in conjunction with the use of SRM 676 as the internal standard. This procedure referenced the phase purity of SRM 674b against that of SRM 676. The basis of the method rests on an analysis of the discrepancy between the results of powder diffraction experiments, which measure the mass of material exhibiting Bragg diffraction, relative to weighing operations, which include all components.

The consideration of a long-count-time X-ray powder diffraction pattern may indicate that the sample is a high purity powder, i.e., no peaks from impurity phases and a background that is consistent with contributions of air scatter from the incident beam and thermal diffuse scatter from the sample. However, the surface region of any crystalline material will not diffract as the bulk due to relaxation of the crystal structure and inclusion of surface reaction products. While this surface layer may only be on the order of a few crystallographic units in thickness, in a finely divided solid it can easily account for several percent of the total mass. The characterization of “phase purity” or “amorphous content” discussed herein is not in the context of a mechanically separable impurity phase, but it is a microstructural characteristic innate to the chemistry and the production history of the SRM feedstock

The QRA of laboratory, divergent beam X-ray powder diffraction (XRPD) data displayed a systematic bias of less than 2 %; however, these results were as precise as those determined from the TOF data. Therefore, the certified phase composition was determined from the TOF data while the homogeneity of the SRM material was verified with Rietveld analyses of XRPD data. It should be noted that the mechanism inducing this bias is not operative in Reference Intensity Ratio (RIR) based methods [7] (for a complete discussion of RIR methods, see [8]). The reported, non-certified, lattice parameters were from the aforementioned Rietveld analyses of the XRPD data. While the XRPD data suffer from centration and penetration errors and, therefore, are not metrological in nature; a linkage is nonetheless established between the reported lattice parameters and the X-ray emission spectrum of Cu, establishing a qualified traceability to the International System of Units (SI) [9].

Ten bottles were selected from the population in accordance to a stratified random protocol. Samples taken from two bottles were combined and admixed with SRM 676 at the 50 % level to yield a total of five samples for TOF neutron diffraction analysis. TOF data were obtained on the High Intensity Powder Diffractometer (HIPD) at the Manuel Lujan, Jr., Neutron Scattering Center (LANSCE), Los Alamos, NM. The samples were contained in 9.5 mm diameter by 50 mm long vanadium cans during the analysis. Each sample was exposed to the neutron beam for 1.3 h with the LANSCE source operating at 70  $\mu$ A proton beam current. Data used for this certification were obtained from detector banks positioned at  $\pm 153^\circ 2\theta$  covering a d-space range of 0.05 nm to 0.48 nm. The run order was randomized on an informal basis. Rietveld refinements using the General Structure Analysis System (GSAS) [10] of the phases in these samples included: scale factors, lattice parameters of the SRM 674b materials (those of SRM 676 were fixed at the certified values) a profile shape function term representing Lorentzian peak broadening [11], atomic positional and thermal parameters, a term for the diffractometer (DIFC), an absorption correction term, and six terms of a background function describing the effects of thermal diffuse and incoherent scattering. The amorphous phase content was determined from the mass fraction ratio determined from the

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<sup>1</sup> Certain commercial materials and equipment are identified in order to adequately specify the experimental procedure. Such identification does not imply a recommendation or endorsement by NIST, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

diffraction experiment relative to that of the weighing operation, with the latter ratio being corrected for the known phase purity of SRM 676.

X-ray diffraction data for homogeneity testing and lattice parameter determination were collected on two specimens removed from each of the ten aforementioned bottles. These specimens also had SRM 676 admixed with them in a 50:50 mass ratio. These XRPD data were collected on a Siemens D5000 diffractometer equipped with a sample spinner, graphite post monochromator and scintillation detector. Copper  $K\alpha_1$  radiation  $\lambda = 0.154\,059\,29\text{ nm}$  [12] was used. The scan range was from  $20^\circ$  to  $155^\circ\,2\theta$  with a step width of  $0.02^\circ$  and a count time of 3.5 s/step. The divergence slit width was  $0.85^\circ$ ;  $2.3^\circ$  incident Soller slits and a  $0.2^\circ$  receiving slit were used. The instrument was calibrated using SRM 660a [13] in conjunction with the *Fundamental Parameters Approach* [14] prior to data collection. For homogeneity testing, lattice parameter determination and microstructural characterization, the XRPD data were analyzed via the *Fundamental Parameters Approach* for Rietveld analyses as implemented in TOPAS, Bruker AXS GmbH [15]. Data analysis used the copper  $K\alpha_1/K\alpha_2$  doublet described by G. Holzer, et al. [12] with a satellite component. Axial divergence was accounted for in using the “full” axial divergence model [16]. The refined parameters included the scale factors, a background represented by a fifth order Chebyshev polynomial with a  $1/x$  term, the lattice parameters of the SRM 674b materials, the intensities and position of the  $K\alpha_2$  and satellite components of the copper  $K\alpha$  emission spectrum, terms indicating the position and intensity of the “tube tails” [17], the secondary Soller slit value in the “full” axial divergence model, specimen displacement, attenuation, and size and strain (when relevant) terms. The reported crystallite size is a volume-weighted dimension, i.e. Scherrer equation, determined from the breadth of a Lorentzian profile following the  $1/\cos\theta$  relation convoluted with the instrument component. The reported strain value,  $(\Delta d/d)_{\text{hkl}}$ , was determined from the breadth of a Lorentzian profile following the  $\tan\theta$  relation convoluted with the instrument component. Assuming the major source of strain is dislocations, the root-mean-square (RMS) strain is 80 % of the quoted strain value [18]. Additional data, using the aforementioned instrument and configuration, were collected from three unaltered specimens of each of the SRM materials for determination of the relative intensity values. The  $I/I_c$  [19] (for a complete discussion see [8]) and relative intensity values were determined by profile fitting of all peaks within the angular range of  $20^\circ$  to  $70^\circ\,2\theta$  using the *Fundamental Parameters Approach* refinement of the non-structural terms as described above.

**Storage:** SRM 674b was bottled under an argon atmosphere to protect against humidity. Although there have been no long-term stability studies on this SRM, the oxides of which it is composed are known to be a stable in the ambient conditions of a typical laboratory. It is, therefore, believed that this SRM is stable after exposure to atmosphere. It is, nonetheless, recommended that the unused portion of the powder be stored in a tightly capped container such as the original bottle or in a manner to afford similar or greater protection against humidity.

**Information Values and Uncertainties:** NIST information values are considered to be of interest to the SRM user, but are not certified because the measurements are not traceable to the SI, or only a limited number of analyses were performed which disallowed imparting plausible uncertainties to the measured values. The information values determined from the aforementioned analyses of XRPD data are presented in Tables 2 through 5. The particle size distributions, determined from a disc centrifuge analyzer, are given in Table 6. The interval defined by a value and its uncertainty is a 95 % confidence interval for the true value of the mean in the absence of systematic error.

Table 2. Lattice Parameters of SRM 674b

Component	a (nm)	c (nm)
ZnO	$0.324\,989\,7 \pm 0.000\,000\,38$	$0.520\,653 \pm 0.000\,035$
TiO <sub>2</sub>	$0.459\,392\,7 \pm 0.000\,004\,4$	$0.295\,887\,5 \pm 0.000\,003\,2$
Cr <sub>2</sub> O <sub>3</sub>	$0.495\,897\,9 \pm 0.000\,002\,7$	$1.359\,592 \pm 0.000\,010$
CeO <sub>2</sub>	$0.541\,165\,1 \pm 0.000\,000\,59$	---

Table 3. Microstructural Parameters for SRM 674b

Component	Crystallite Size L (nm)		Microstrain
ZnO	201.4	$\pm 2.5$	---
TiO <sub>2</sub>	281.6	$\pm 9.9$	$0.064 \pm 0.002$
Cr <sub>2</sub> O <sub>3</sub>	380.2	$\pm 14.4$	$0.045 \pm 0.001$
CeO <sub>2</sub>	380.6	$\pm 4.5$	---

Table 4. I/I<sub>c</sub> Values for SRM 674b

Component	I/I <sub>c</sub>		
ZnO	4.95	±	0.01
TiO <sub>2</sub>	3.44	±	0.01
Cr <sub>2</sub> O <sub>3</sub>	1.97	±	0.02
CeO <sub>2</sub>	12.36	±	0.09

Table 5. Relative Intensity Values of SRM 674b

ZnO			TiO <sub>2</sub>		
hkl	Angle	Rel I	hkl	Angle	Rel I
1 0 0	31.76	61.30 ± 2.34	1 1 0	27.45	100.0 ----
0 0 2	34.41	37.24 ± 2.10	1 0 1	36.09	37.70 ± 1.50
1 0 1	36.25	100.0 ----	2 0 0	39.20	5.96 ± 0.12
1 0 2	47.53	22.29 ± 0.66	1 1 1	41.25	18.70 ± 0.48
1 1 0	56.59	37.72 ± 1.44	2 1 0	44.05	7.46 ± 0.25
1 0 3	62.85	30.28 ± 1.14	2 1 1	54.32	55.14 ± 1.58
2 0 0	66.37	5.25 ± 0.24	2 2 0	56.63	17.48 ± 0.31
1 1 2	67.94	27.13 ± 0.12	0 0 2	62.76	6.94 ± 0.40
2 0 1	69.08	14.12 ± 0.32	3 1 0	64.05	8.03 ± 0.21
			3 0 1	69.00	19.41 ± 0.62
			1 1 2	69.80	8.96 ± 0.58

  

Cr <sub>2</sub> O <sub>3</sub>			CeO <sub>2</sub>		
hkl	Angle	Rel I	hkl	Angle	Rel I
0 1 2	24.52	66.71 ± 1.71	1 1 1	28.61	100.0 ----
1 0 4	33.62	100.0 ----	2 0 0	33.14	27.21 ± 0.46
1 1 0	36.22	81.27 ± 4.78	2 2 0	47.54	54.21 ± 0.56
0 0 6	39.77	7.36 ± 0.93	3 1 1	56.39	43.58 ± 0.60
1 1 3	41.50	31.64 ± 0.60	2 2 2	56.14	8.29 ± 0.38
2 0 2	44.22	5.24 ± 0.25	4 0 0	69.46	8.03 ± 0.25
0 2 4	50.24	39.64 ± 1.10			
1 1 6	54.86	96.42 ± 0.64			
1 2 2	58.42	8.17 ± 0.74			
2 1 4	63.48	31.06 ± 1.55			
3 0 0	65.13	39.31 ± 1.43			
1 0 10	72.95	20.88 ± 1.53			

Table 6. Particle Size Data for SRM 674b Determined Using a Disk Centrifuge Analyzer

Mass Percent Less Than (μm)	Components			
	ZnO	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	CeO <sub>2</sub>
10 %	0.22	0.41	0.34	0.53
16 %	0.28	0.55	0.38	0.65
50 %	0.58	0.93	0.56	1.13
84 %	1.15	1.38	1.05	1.91
90 %	1.55	1.66	1.45	2.18

## REFERENCES

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*Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail [srminfo@nist.gov](mailto:srminfo@nist.gov); or via the Internet at <http://www.nist.gov/srm>.*